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PROCESS FOR PREPARATION OF 1, 3-PROPANEDIOL

Field Of The Invention

This invention relates to a process for preparing 1, 3-propanediol from 3-hydroxypropionic acid or derivatives thereof.

Background Of The Invention

Various methods for producing 1, 3-propanediol are known. Included within such methods is the production of 1, 3-propanediol by the catalytic hydrogenation of methyl 3-hydroxypropionate in the presence of a copper zinc oxide catalyst, as shown in U.S. Patent No. 6,191,321. It is also known from U.S. Patent No. 3,770,837 that 1, 3-propanediol may be prepared by hydrogenating beta-hydroxypropionic acid or beta-propiolactone in the presence of rhenium black catalyst. Furthermore, it is described in U.S. Patent No. 6,025,184, that 1, 3-propanediol may be produced from glucose by a fermentation procedure.

Summary Of The Invention

It is accordingly an object of the present invention to provide a new process for preparing 1, 3-propanediol.

It is a further object of this invention to provide a new process for preparing 1, 3-propanediol in good yield.

These and other objects and advantages of the present invention will be apparent to those skilled in the art from the following detailed description and claims.

In accordance with the present invention, it has been found that the above and still further objects are achieved by hydrogenating 3-hydroxypropionic acid, or esters of the acid or mixtures, in the presence of a specific catalyst, in a liquid phase, to prepare 1, 3-propanediol. The catalysts that are used in the process of the present

invention are ruthenium metal, or compounds of ruthenium, supported or unsupported, alone or in combination with at least one or more additional metal(s) selected from molybdenum, tungsten, titanium, zirconium, niobium, vanadium or chromium, or compound of the additional metal(s).

The 1, 3-propanediol product is a known compound having many applications, and the products produced herein are useful in such applications.

Another object of the invention is to provide a process that includes using 3-hydroxypropionic acid that has been produced via a fermentation process that can utilize genetically engineered organisms, such as bacteria, yeast, or fungi. The biologically produced 3-hydroxypropionic acid generally is in the form of a salt, such as an ammonium salt, in the resulting fermentation both. To separate the ammonium salt and form the free acid an organic extractant is added to the reactor, followed by heating.

Detailed Description Of The Invention

The process of the present invention relates to the preparation of 1, 3-propanediol, by hydrogenating 3-hydroxypropionic acid, or esters of the acid or mixtures of the acid and ester, in the presence of a specific catalyst, in a liquid phase.

The present invention provides a process for producing 1, 3-propanediol from 3-hydroxypropionic acid or esters of 3-hydroxypropionic acid having the formula, $HOCH_2\ CH_2\ CO_2R$, wherein R is a C_1-C_{20} alkyl group, linear or branched, optionally substituted by halogen, alkoxy, amino, alkylamino, or hydroxyl groups, or a $C_1 - C_{20}$ aryl group, linear or branched, optionally substituted by halogen, alkoxy, amino, alkylamino, or hydroxyl groups. Exemplary of the esters of 3-hydroxypropionic acid suitable for use herein are $C_1 - C_5$ esters of 3-hydroxypropionic acid.

The catalysts that are used in the process of the present invention are ruthenium metal or compounds of ruthenium, either supported or unsupported, alone, or in combination with at least one or more additional metal(s) selected from molybdenium, tungsten, titanium, zirconium, niobium, vanadium or chromium, or a compound of the additional metal(s).

The compounds of both the ruthenium metal, and the additional metal(s), include oxides, hydroxides, halides, nitrates, carboxylates and the like. Indeed, any compound of the ruthenium and the additional metal is suitable for use herein provided that the hydrogenation of the 3-hydroxypropionic acid, in liquid phase, to prepare 1, 3-propanediol, may be successfully achieved.

The ruthenium metal or compound thereof, and/or the additional metal(s), or compound thereof, may be utilized in supported or unsupported form. If utilized in supported form, the method of preparing the supported catalyst is not critical and can be any technique such as impregnation of the support or deposition on the support.

These techniques are well known and require no description. The metal in the supported catalyst comprises up to about 50% by weight of the catalyst, particularly up to about 20% by weight of the catalyst.

Any suitable support may be utilized provided that the preparation of 1, 3-propanediol by the present process may be achieved. Supports that may be used herein include, but are not limited to, alumina, titania, silica, zirconia, carbons, carbon blacks, graphites, silicates, zeolites, aluminosilicate zeolites, aluminosilicate clays, and the like.

When two or more catalysts are used they are added as distinct compounds that are not in the form of an adduct or reaction product. The catalysts however, can be pre-mixed and added simultaneously. The catalyst concentration used in the

present process ranges, from about 0.01 to about 100% by weight of ruthenium, based on the weight of 3-hydroxypropionic acid reactant. When an additional metal catalyst is used in combination with the ruthenium catalyst, the amount of the additional metal catalyst utilized ranges preferably, from about 1 to about 100% by weight, based on the weight of the 3-hydroxypropionic acid reactant.

The hydrogenation process of the present invention is carried out in liquid phase. The liquid phase includes water, organic solvents that are not hydrogenatable, such as any aliphatic or aromatic hydrocarbon, alcohols, ethers, toluene, decalin, dioxane, diglyme, n-heptane, hexane, xylene, benzene, tetrahydrofuran, cyclohexane, methylcyclohexane, and the like, and mixtures of water and organic solvent(s).

The hydrogenation process of the present invention may be carried out batch wise, semi-continuously, or continuously.

The present process may be carried out in any suitable apparatus. Exemplary of such apparatus are stirred tank reactors, trickle-bed reactors, high pressure hydrogenation reactors, and the like.

The hydrogen containing gas utilized in the present process is, typically, commercially pure hydrogen. However, it is not essential that the hydrogen containing gas be commercially pure. The hydrogen containing gas is usable if nitrogen, gaseous hydrocarbons, or oxides of carbon, and similar materials, are present in the hydrogen containing gas.

The hydrogenation process of the present invention is generally carried out at a temperature ranging from about 20° to about 250° C, more particularly from about 100° to about 200° C. Further, the hydrogenation process of the present invention is generally carried out in a pressure range of from about 20 p.s.i. to about 4000 p.s.i. (pounds per square inch), and more particularly, in a pressure range of from about 500

p.s.i. to about 2000 p.s.i. There is no specific residence time required for the present hydrogenation reaction, other than the residence time be adequate to allow the intended product to be produced. More particularly, the residence time for the present hydrogenation ranges from about 1 to about 10 hours.

It has been noted that carrying out the present hydrogenation process may result in the production of reaction by-products, such as n-propanol, acrylic acid and others. Recovery of the reaction by-products that are valuable, is achieved by any method conventional in the art.

The invention will be more readily understood by reference to the following examples. There are, of course, many other forms of this invention which will become obvious to one skilled in the art, once the invention has been fully disclosed, and it will accordingly be recognized that these examples are given for the purpose of illustration only, and are not to be construed as limiting the scope of this invention in any way.

EXAMPLES

In the following examples, the products produced by the hydrogenation processes were analyzed using a Waters 1525 Binary HPLC pump, equipped with a Waters 717 plus Autosampler, and Waters 2410 Refractive Index and Waters 2487 Dual Lambda Absorbance detectors, having a Bio-Rad HP87-H column, 0.004 N sulfuric acid as the mobile phase, a flow rate of 0.6ml/min, and a column temperature of 60° C.

DESCRIPTION OF GC PARAGRAPH, AND

DESCRIPTION OF PMC MATERIAL

The 3-hydroxypropionic acid was purchased as a 30% solution from TC[1], Oregon. This product, however, contains approximately 20% monomer and the

remaining 10% of the 3-hydroxypropionic acid content is in the form of various dimers.

The protocol for the gas chromatograph was as follows: A J & W DB-Waxetr 30m x 32mm 0.5um film column was used with an internal oven temperature at 90°C with a 20°C/min increase to a final temperature of 200°C. The sample was maintained at 200°C for about 12.5 minutes prior to injection. Retention times for 1,3 propandion were about 6.8 minutes and about 15.8 minutes for 3-hydroxypropionic acid.

Examples 1-22

Examples 1-22 of the present invention were carried out in the following manner. A catalytic hydrogenation of a solution of 20% 3-hydroxypropionic acid (herein 3-HP) in water was carried out in a stirred autoclave bench top reactor. In the examples, the autoclave reactor was a Parr reactor, available from Parr Instrument Company, Moline, Illinois. The concentrations of reactants and resultant products were analyzed by HPLC and, GC. An aqueous solution of the 3-hydroxypropionic acid (3-HP) in water, the liquid phase, and the catalyst were charged into the autoclave reactor. The reactor was flushed three times with hydrogen. The reactor was then pressurized to about 200 p.s.i. of hydrogen. The reactor was heated to the desired temperature, and, then, pressurized to the desired hydrogen pressure. The mixture of reactants was stirred, at the desired temperature and hydrogen pressure, in the autoclave reactor for a desired period of time. Thereafter, the autoclave reactor was cooled to room temperature, and the hydrogen pressure was released. The resultant reaction mixture was separated by centrifugation and filtration, and the obtained aqueous solution was analyzed by HPLC and GC techniques, to determine

the concentrations of the reactants and the products that were prepared. The processing conditions, and the product data are reported for the examples

in Table 1, wherein a ruthenium catalyst is solely utilized, and in Table 2, wherein the catalyst used is a combination of a ruthenium catalyst and an additional metal-containing catalyst.

TABLE 1

Preparation of 1, 3-propanediol (1, 3-PDO) by Hydrogenating 3-hydroxypropionic Acid (3-HP)

Example	20% 3-HP in water, g	Liquid Phase, g	Catalyst, g	Temp. °C	Pressure p.s.i.	Reaction Time, Hours	1, 3-PDO yield, %
1	10	None	3.25g Ru/C[2]	100	1500	16	47
2	10	40gA[1]	3.20g Ru/C[2]	100	1500	16	41
3	21	33gA[1]	6.28g Ru/C[2]	100	1500	20	34
4	11	40gA[1]	6.63g Ru/C[2]	80	2100	20	31
5	11	42g xylene	6.79g Ru/C[2]	80	2100	20	26
6	10	41g heptane	6.48g Ru/C[2]	80	2100	20	36

(1) - A is ISOPAR K $C_{10}-C_{11}$ paraffin available from Exxon Mobil Company
(2) - Ru/C is about 5% ruthenium metal on carbon having about 50% water. This product is available

TABLE 2

Preparation of 1, 3-Propanediol (1, 3-PDO) by Hydrogenating 3-hydroxypropionic Acid (3-HP)

Example	20% 3-HP in water, g	Liquid Phase, g	Catalyst, g	Temp °C
7	21	30g water	3.27g Ru/C[2] and 1.24g MoO_2	150
8	10	41g A[1]	1.64g Ru/C[2] and 0.63g MoO_2	150
9	21	30g A[1]	6.59g Ru/C[2] and 0.35g MoO_3	100
10	20	31g A[1]	6.47g Ru/C[2] and 0.35g MoO_3	80
11	10	40g A[1]	1.69g Ru/C[2] and 0.31g MoO_3	100
12	11	41g A[1]	3.39g Ru/C[2] and 0.32g MoO_3	100
13	10	40g A[1]	3.23g Ru/C[2] and 0.61g MoO_3	120
14	11	47g A[1]	3.5g Ru/C[2] and 0.67g MoO_2	120
15	10*	40g A[1]	1.75g Ru/C[2] and 0.66g MoO_2	150
16	10	41g A[1]	1.63g Ru/C[2] and 0.61g Mo	150
17	10	40g A[1]	1.62g Ru/C[2] and0.62g MoO_2	135
18	11	46g A[1]	3.59g Ru/C[2] and 0.68g WO_3	120
19	11	40g A[1]	3.46g Ru/C[2] and 0.66g ZnO_2	100
20	10	41g A[1]	3.28g Ru/C[2] and 0.32g TiO_2	100
21	11	41g A[1]	1.63g Ru/Al_2O_3 and 0.33g MoO_2	100
22	10	40g A[1]	1.7g Ru/C[2] and 0.61g NbO_2	150

TABLE 2 (cont)

Preparation of 1, 3-Propanediol (1, 3-PDO) by Hydrogenating 3-hydroxypropionic Acid (3-HP)

Example	Pressure p.s.i.	Reaction Time Hours	1, 3-PDO yield, %
7	1500	3	60
8	1500	3	56
9	1500	20	60
10	1500	20	37
11	1500	20	49
12	1500	20	66
13	1500	3	42
14	1500	3	48
15	1500	3	46
16	1500	3	57
17	1500	6	61
18	1500	3	19
19	1500	20	26
20	1500	20	42
21	1500	20	16
22	1500	3	31

* - The starting reactant of Example 15 was a solution of 29% 3-HP in water
(1) - A is ISOPAR K $C_{10} - C_{11}$ paraffin, available from Exxon Mobil Company
(2) - Ru/C is about 5% ruthenium metal on carbon having about 50% water available from PMC Precious Metals Corporation, Sevierville, Tennessee.

Example 23

The procedures of Examples 1 and 7 are followed except that the carbon support of the ruthenium/carbon catalyst is replaced with a silica support and a zeolite support respectively. It is expected that 1, 3-propanediol will be obtained in good yield.

Example 24

The procedure of Example 7 is followed except that the molybdenum oxide is replaced by vanadium oxide and chromium oxide, respectively. It is expected that 1, 3-propanediol will be obtained in good yield.

Example 25

The procedures of Examples 1 and 7 are followed except that the Ru/C supported catalyst is replaced by unsupported ruthenium catalyst. It is expected that 1, 3-propanediol will be obtained in good yield.

Example 26

The procedures of Examples 1 and 7 are followed except that the Ru/C supported catalyst is replaced by carbon supported ruthenium oxide catalysts. It is expected that 1, 3-propanediol will be obtained in good yield.

Example 27

The procedures of Examples 2 and 8 are followed except that the ISOPAR K paraffin liquid phase was replaced by hydrocarbon, alcohol, aromatic compounds such as xylene and ether, respectively. It is expected that 1, 3-propanediol will be obtained in good yield.

Example 28

The procedures of Examples 6 and 7 are followed except that the solution of 20% 3-HP in water, is replaced by methyl 3-hydroxypropionate in alcohol, as the starting reactant. It is expected that 1, 3-propanediol will be obtained in good yield.

The invention has been described above in detail with particular reference to specific embodiments thereof, but it will be understood that variations and modifications other than as specifically described herein can be effected within the spirit and scope of the invention.